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Sorptional Dehydration and Thermochemical Sintering of Converter Sludge

S. N. Kuznetsov*, M. B. Shkoller, E. V. Protopopov***, M. V. Temlyantsev****, and S. V. Feiler*******

Siberian State Industrial University, Novokuznetsk
**e-mail: mchmsis@mail.ru*
***e-mail: chkoller@mail.ru*
****e-mail: protopopov@sibsiu.ru*
*****e-mail: uchebn_otdel@sibsiu.ru*
******e-mail: feyler@rdtc.ru*

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Abstract—Global steel output in 2016 exceeded 1.6 billion t, of which more than 1.2 billion t was produced in converters. The smelting of 1 t of steel produces up to 25 kg of fine dust, depending on various factors. This dust contains up to 65% iron, in oxide form. Recycling of the waste formed in steel production costs half or a third as much as the preparation of ore concentrates. For the recycling of converter sludge, methods of conditioning wet wastes by isothermal sorptional dehydration and subsequent thermochemical sintering have been developed. The adsorbent used in the present work is the solid residue from lignite pyrolysis: fine-grain lignite semicoke produced by a pilot plant at the Berezovskii-1 mine. The lignite-semicoke samples produced have a highly developed pore structure and correspondingly are characterized by excellent sorptional and energy properties. The granulometric composition of lignite semicoke is practically the same as that of the sludge. At the same time, the density of the lignite-semicoke particles is 2.5 times less than that of the sludge particles, even when the pores of the semicoke are completely filled with adsorbed moisture. On mixing the lignite semicoke and converter sludge, the semicoke absorbs moisture. The resulting mixture is highly friable, whereas the moisture adsorbed in the pores passes to the bound state and becomes an active participant in redox processes. As a result of the experiments, new material containing up to 39% Fe_{met} and 49% C is obtained. On that basis, an effective technology may be developed for the utilization of converter sludge to produce ferrocoke that may be employed as a fuel and reducing agent in blast furnaces and smelters. The proposed technology does not require complex mechanical and thermal dehydration and briquetting with binder.

Keywords: oxygen converters, ferrocoke, lignite semicoke, converter sludge, sorptional dehydration, thermochemical sintering, redox processes, recycling

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Despite the increasing use of nonmetallic materials and composites, steel remains the leading structural material in terms of its properties and its production volume. Traditionally, most steel is produced in oxygen converters [1–6].

Depending on the batch composition, the converter design, and the smelting technology, the production of 1 t of steel is associated with the generation of 12–25 kg of fine dust. About 80% of the dust is removed from the smokestack gases and 72% of the dust is utilized [7, 8].

Converter sludge is a valuable source of iron. In particular, the converter sludge from AO EVRAZ ZSMK contains 57–65% Fe. Most is in the form of the oxide Fe_2O_3 [9, 10].

Recycling of the converter sludge provides an additional source of iron; disposes of fine waste particles in an environmentally safe manner [11, 12]; reduces resource consumption; and lowers the cost of steel production [10, 12, 13]. Accordingly, the development of efficient recycling technologies is a high priority in steel production.

Despite its benefits, the processing of converter sludge also creates some problems. In particular, iron-bearing materials are generally introduced in the blast furnace or the converter in chunks, and consequently recycled waste (rolling scale, dust, dehydrated sludge, etc.) is traditionally added to sintering batch [7]. However, adding large quantities of fine particles to the sintering batch tends to reduce the productivity in sintering and to impair the strength of the sinter produced [9].

An alternative might be the briquetting of fine iron-bearing waste.

The benefits of briquetting are as follows: conditioned products with controllable dimensions and properties may be obtained from waste of different chemical composition and properties; the density of the friable materials may be increased; caking and clogging of fine waste particles in the bunkers and dosing system may be prevented; and the loss of dust in transportation and utilization may be reduced [9]. The components may be more efficiently used in briquet form than in any other state (in fine or polydisperse fractions or in sorted form). In comparison with sintering, the briquetting of iron-bearing wastes offers the following advantages [9].

(1) The briquets are of the same shape and mass, have high iron content, density, and strength, and are easy to transport.

(2) The recycled product may be 20–25% or more of the total batch flux in sintering, as against only 2–6% at a briquet plant.

(3) All the oxygen in the briquet remains active, whereas it is bound in silicates in sinter. That is especially important for blast-furnace use.

(4) Briquetting has no environmental impact. It is waste-free and does not require high temperatures.

(5) Any proportion of hydrocarbon filler may be added to the briquet in order to activate the processes in the metallurgical furnace (additions of reducing agent, carburizing agent, fuel, etc.).

(6) All types of fine metallurgical waste may be employed.

However, converter sludge must be dehydrated before briquetting. As a rule, existing dehydration methods are cumbersome and energy-intensive and require preliminary removal of moisture (to levels of 20–25%) by mechanical methods (compaction, filtration) and thermal drying [9, 10, 13–15]. That allows the material to be brought to a dry state. However, considerations of fire and explosion safety strictly limit the intensity of high-temperature processes [13–15].

Another constraint on the use of converter sludge in blast-furnace batch is its content of zinc oxides, which shorten the life of the furnace housing and lining.

Note that the replacement of natural resources by wastes from later stages of metallurgical processing increases the economic and environmental benefits of waste recycling in metallurgy [9, 16–19]. For the recycling of converter sludge, a method of conditioning very wet wastes on the basis of sorptional dehydration and thermochemical sintering has been developed [20–22]. In Fig. 1, we show the basic system.

The converter sludge from store *1* is sent to compacter *2* and then to mixing and adsorption unit *5* for contact with fine-grain lignite semicoke, which serves as the adsorbent. Then the semicoke–sludge mixture is sent for separation in pneumatic classification system *7*. From there, the lighter lignite semicoke is sent through a dust-separation system (cyclone *6* and bag filter *8*) to bunker *9*, from which it is taken to meet energy needs. The air from which the dust has been removed is released to the atmosphere. The heavier sludge from the pneumatic classification system passes through a dosing unit to mixer *12*, to which coking coal is added in dosed quantities from bunker *11*. In rotating-hearth furnace *13*, the resulting sludge–coal mixture undergoes thermooxidative coking.

The ferrocoke obtained at 1100–1150°C (Fig. 2) is cooled in dry-quenching system *15*, sorted into three classes (0–10 mm, 10–25 mm, and +25 mm), and sent to waste-heat boiler *17*. On combustion of the gaseous products above the batch bed in the rotating-hearth furnace, heat is generated for use in coking. At the same time, the reduction of the iron oxides to Fe_{met} and the zinc oxides to Zn_{met} ends in the final stage of coking at 1050–1100°C. The temperature at which reduction of the zinc oxide begins is 1070°C, according to [20]. The combustion products are sent together with zinc vapor from the furnace to condenser *18*, where liquid metallic zinc is collected. The remaining gaseous products are sent to gas-turbine system *14* for subsequent use.

In the present work, we conduct experiments on the dehydration and sintering of converter sludge so as to improve the technology.

DEHYDRATION OF CONVERTER SLUDGE

We investigate sorptional dehydration for converter sludge from AO EVRAZ ZSMK containing 50.0 wt % moisture. The composition of the dry converter sludge is as follows: 46.81 wt % Fe_{tot}, 64.05 wt % Fe_2O_3, 1.82 wt % FeO, 4.59 wt % MgO, 16.68 wt % CaO, 5.75 wt % SiO_2, 0.19 wt % K_2O, 0.069 wt % V_2O_5, 0.10 wt % Cr_2O_3, 0.63 wt % C, 0.24 wt % S, 1.11 wt % ZhO, 0.061 wt % CuO, 0.11 wt % PbO, 1.08 wt % MnO, 1.93 wt % Al_2O_3, 0.88 wt % Na_2O, 0.32 wt % P_2O_5, and 0.21 wt % TiO_2. No metallic iron (Fe_{met}) is present.

The granulometric composition of the thermally dried slurry is determined by means of a Malvern-2000 instrument at the Materialovedenie Collective-Use Center, Siberian State Industrial University.

Analysis of the granulometric composition shows that the solid component consists of small particles (0.5–1000 μm); the maximum of the granulometric curve is close to 500 μm. The absorbent used in the solid residue from lignite pyrolysis: fine-grain lignite semicoke produced by Termokoks-KS on a pilot plant at the Berezovskii-1 mine [21].

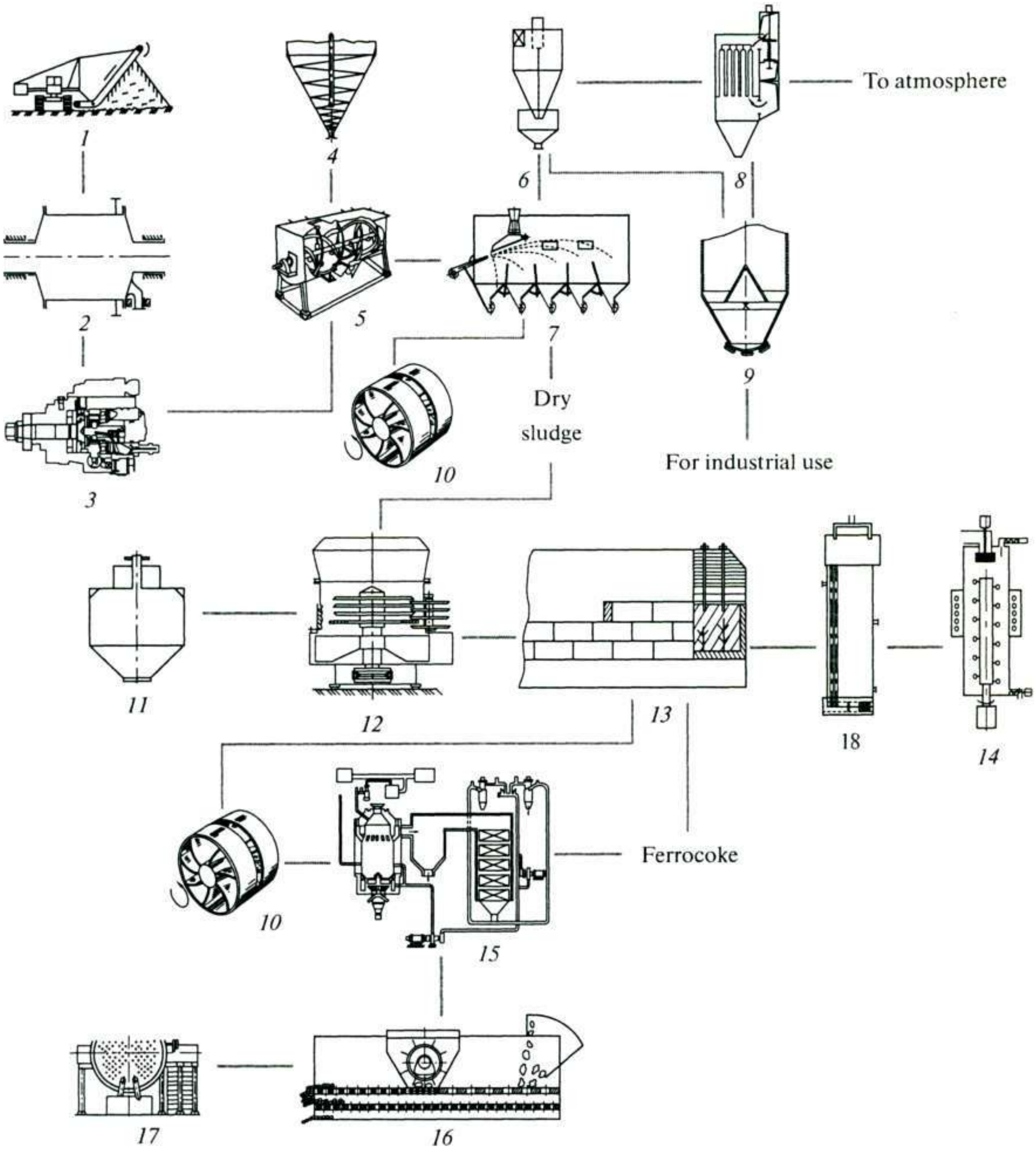

Fig. 1. Conditioning of wet converter sludge by sorptional dehydration and thermochemical sintering: (*1*) sludge store; (*2*) consolidation unit; (*3*) sludge pump; (*4*) bunker for lignite semicoke; (*5*) mixing and sorption unit; (*6*) cyclone; (*7*) pneumatic classification system; (*8*) bag filter; (*9*) bunker for wet lignite semicoke; (*10*) blower; (*11*) bunker for GZh + Zh coal; (*12*) mixer; (*13*) coke oven with rotating hearth; (*14*) gas-turbine system; (*15*) unit for dry quenching of coke; (*16*) sorting unit for semicoke; (*17*) waste-heat boiler; (*18*) condenser.

The lignite-semicoke samples produced have a highly developed pore structure and correspondingly are characterized by excellent sorptional and energy properties [20, 21].

The volume of micropores in the lignite semicoke is more than ten times that in coke from regular coal. Hence, the sorptional capacity of lignite semicoke is close to that of traditional active carbon. The sorptional capacity of lignite semicoke is slightly less than that of ABG-D sorbent (activated carbon, Technical Specifications TU 600209591-443–95) and markedly exceeds that of DAK sorbent (activated charcoal, Technical Specifications TU 0321002-51577712). That indicates the possibility of using lignite semi-

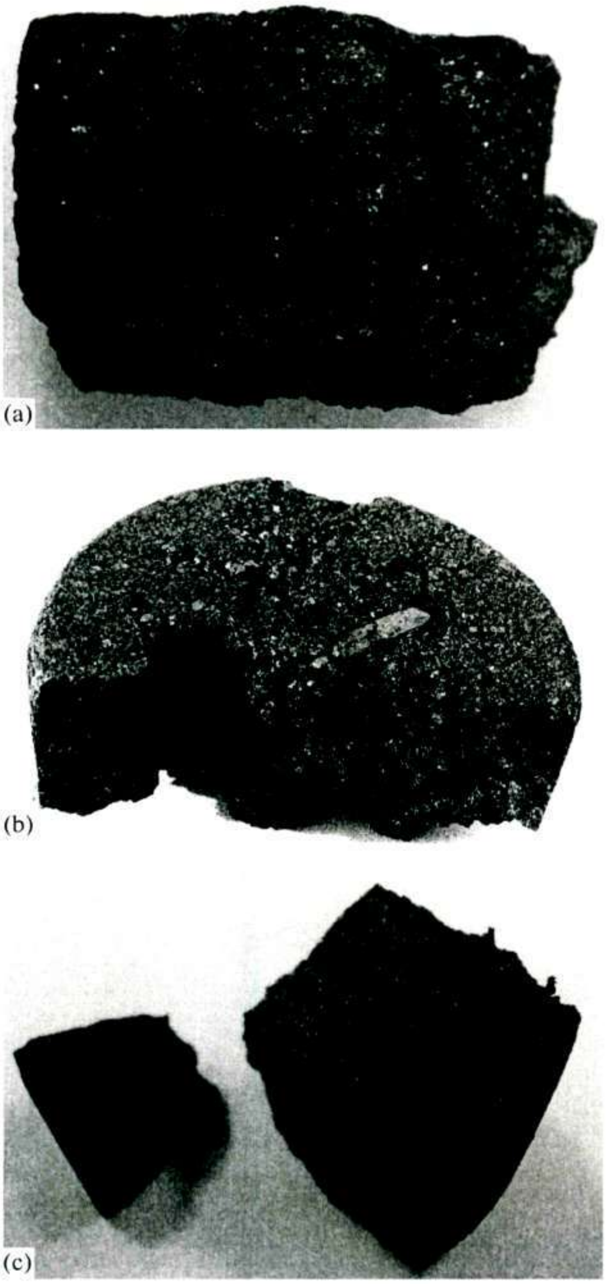

Fig. 2. Samples of ferrocoke.

coke to modify the technological properties of coal mixtures.

The granulometric composition of lignite semicoke is practically the same as that of the sludge. At the same time, even when the pores of the semicoke are completely filled with adsorbed moisture, the density of the lignite-semicoke particles (1.42 g/cm^3) is less than that of the sludge particles (3.8 g/cm^3) by a factor greater than 2.5.

The characteristics of the lignite semicoke (from the Berezovskii-1 mine) are as follows:

Total moisture content, %	3.0
Ash content (dry state), %	9.7
Yield of volatiles, %	9.9
Elementary composition (combustible mass), %:	
carbon	92.8
oxygen	4.45
hydrogen	1.52
sulfur (dry state), %	0.24
phosphorus (dry state), %	0.026
Gross calorific value, MJ/kg	32.8
Net calorific value (working state), MJ/kg	28.0–28.5
Sorptional activity (for iodine), %	At least 42
Total pore volume, cm^3/g	0.47
Specific surface of pores, m^3/g	500
Actual density, kg/m^3	1880
Apparent density, kg/m^3	974
Packing density, kg/m^3	550

As we see, lignite semicoke is a high-calorific product characterized by ash and sulfur content and by a highly developed and accessible pore structure.

In studying dehydration, we assess the friability S of the material (State Standard GOST 25139–93). In determining the semicoke/sludge mass ratio required to obtain a friable mixture, we need to know the moisture content of the sludge and the sorptional capacity of lignite semicoke. Preliminary calculations show that, when the moisture content of the sludge is 50 wt %, the sludge/semicoke mass ratio required is 1 : 1.3. Experiments confirm this result.

The moisture content W and friability S of the materials considered are as follows:

Material	W, %	S, g/s
Initial sludge (mud consistency)	50.0	0
Lignite semicoke	3.0	25.28
Thermally dried sludge	1.35	0
Mixture of sludge and lignite semicoke	16.55	33.34

On mixing the lignite semicoke and converter sludge, the semicoke absorbs the moisture. The resulting mixture is highly friable. This is important for transport purposes. The moisture adsorbed in the pores passes to the bound state and becomes an active participant in redox processes.

After pneumatic separation of the sludge and the lignite semicoke, the semicoke may be employed as a

Table 1. Characteristics of the coal concentrates

Concentrate	Technical analysis				Plastometry		Petrography		
	W^r, %	A^d, %	V^{daf}, %	S^d, %	X, mm	Y, mm	Vt, %	S_R	R
GZh + Zh	10.5	7.8	38.0	0.56	17	24	85.0	0.560	0.864
Zh	8.6	8.1	38.2	0.67	−2	34	93.0	0.045	0.853

fuel or for other purposes. The sludge is sent for thermochemical sintering to obtain ferrocarbon chunks.

Pneumatic separation of the mixture is possible because, although the granulometric composition of lignite semicoke is practically the same as that of the sludge, they differ in density by a factor of around 2.5.

BRIQUETTING OF SLUDGE

Briquetting offers broad scope for the utilization of fine-grain wastes. It is also promising in terms of the generation of a metallic product, since reducing agents may be introduced in the briquetting batch. A benefit of briquets is that their open porosity is less than that of reduced pellets and so they are less susceptible to active secondary oxidation in the atmosphere [9].

Briquetting is less expensive than sintering or the production of roasted pellets. The briquetting of fine wastes is less challenging than those other methods, since the quality of the briquets is less dependent on the granulometric composition and moisture content of the initial material. In addition, the size, shape, and chemical composition of the briquets may readily be regulated by selecting the size and shape of the matrix cells, selecting the binder, and introducing additives [9].

In the proposed system, we use thermochemical sintering of slurry mixed with coking coal in the course of coking in an annular furnace with a rotating hearth, so as to obtain special forms of coke [23].

We consider two mixtures:

(1) 50% GZh + Zh coal concentrate from Kuznetskaya enrichment facility and 50% converter sludge;

(2) 50% Zh coal concentrate from the Mezhegei field and 50% converter sludge.

The Table 1 presents the characteristics of the coal concentrates.

In determining the mass ratio of the mixture components, we take into account that the converter sludge acts as a lean additive in the coking coal, with a high yield of volatiles, and that good clinkering properties of the mixture are required to obtain strong briquets. The thickness of the plastic layer is 10 and 17 mm for samples 1 and 2, respectively.

To reproduce the industrial coking process in annular furnaces with a rotating hearth, we heat the experimental mixtures to 730°C in a plastometric-analysis system. As a result of the removal of volatiles from the coal component of the samples, the sludge content rises to 56–57%. The FeO content in the sludge increases from 1.82 to 14.3% and 2.03% Fe_{met} appears. The content of zinc oxides is 0.48%.

After plastometric analysis, the samples are heated for 30 min in a Tamman furnace to the final coking temperature (1050–1100°C). Roasting is accompanied by solid-phase reduction of the iron. In particular, the Fe_{tot} content is 84.9% in sample 1 and 94.4% in sample 2.

The material obtained in the experiments is an analog of ferrocoke (Fig. 2). Ferrocoke production was developed in the 1930s with the goal of combining iron-ore dust unsuitable for blast-furnace use with bituminous or quasi-bituminous coal. The resulting ferrocoke may be used in coke batteries. It may be classified as a ferrocarbon composite subjected to heat treatment outside the smelter. Ferrocoke mainly contains metallic iron and carbon [24–26]. The material obtained in our experiments contains 35–39% Fe_{met} and 45–49% C. The ZnO content is no more than 0.017%. Its compressive strength is 2.8 MPa.

The use of ferrocoke in blast furnaces and especially in converters is of practical interest. It may serve as an additional fuel and reducing agent when using a process that includes liquid-phase reduction.

CONCLUSIONS

Analysis of the conditioning of wet converter sludge by sorptional dehydration and subsequent thermochemical sintering permits the development of an effective technology whose product may be used in blast furnaces and smelters as a fuel and reducing agent.

The proposed technology does not require complex mechanical and thermal dehydration or briquetting with binder.

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REFERENCES

1. Protopopov, E.V. and Feyler, S.V., Analysis of current state and prospects of steel production development, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2016, vol. 150, pp. 1–8.

2. Yuzov, O.V., Sedykh, A.M., and Afonin, S.Z., Trends in development and economic indicators of the Russian steel industry, *Stal'*, 2013, no. 4, pp. 72–77.
3. Brun, L., *Overcapacity in Steel. China's Role in a Global Problem*, Durham: Duke Univ. Press, 2016.
4. Mutumi Ohji, Recent trends and future tasks in steelmaking technology in Japan, *ISIJ Int.*, 1996, vol. 36, pp. S2–S5.
5. Budanov, I.A. and Ustinov, V.S., Prospective development of metallurgical production in Russia, *Chern. Metall.*, 2014, no. 5, pp. 3–12.
6. Springorum, D., The management of research and technology in the German steel industry with respect to the European Union, *ISIJ Int.*, 1998, vol. 38, pp. 935–942.
7. Tolochko, A.I., Slavin, V.I., Suprun, Yu.M., and Khairutdinov, R.M., *Utilizatsiya pyli i shlamov v chernoi metallurgii* (Utilization of Dust and Sludge in Ferrous Metallurgy), Moscow: Metallurgiya, 1990.
8. Su, F., Lampinen, H.-O., and Robinson, R., Recycling of sludge and dust to the BOF converter by cold bonded pelletizing, *ISIJ Int.*, 2004, vol. 44, pp. 770–776.
9. Kuznetsov, S.N., Volynkina, E.P., Protopopov, E.V., and Zorya, V.N., *Metallurgicheskie tekhnologii pererabotki tekhnogennykh mestorozhdenii, promyshlennykh i bytovykh otkhodov* (Metallurgical Technologies for Processing of Technogenic Deposits, Industrial and Household Wastes), Novosibirsk: Sib. Otd., Ross. Akad. Nauk, 2014.
10. Dobrovol'skii, I.P., Chernyavskii, I.Ya., Abyzov, A.N., and Kozlov, Yu.E., *Pererabotka i utilizatsiya promyshlennykh otkhodov Chelyabinskoi oblasti* (Recycling and Utilization of Industrial Wastes in the Chelyabinsk Oblast), Chelyabinsk: Chelyab. Gos. Univ., 2000.
11. Gostenin, V.A., Eliseev, Yu.P., Kovalenkova, E.Yu., and Neverovskaya, I.P., Slurry processing to produce iron concentrate, *Steel Transl.*, 2016, vol. 46, no. 4, pp. 301–302.
12. Ravich, B.M., Okladnikov, V.P., Lygach, V.N., and Menkovskii, M.A., *Kompleksnoe ispol'zovanie syr'ya i otkhodov* (Complex Use of Raw Materials and Wastes), Moscow: Khimiya, 1988.
13. Baryshnikov, V.G., Gorelov, A.M., Papkov, G.I., et al., *Vtorichnye material'nye resursy chernoi metallurgii* (Secondary Material Resources for Ferrous Metallurgy), Moscow: Ekonomika, 1986, vol. 2.
14. Dobrovol'skii, I.P. and Rymarev, P.N., A promising technology for processing slurries from converter production of steel and oily scale, *Vestn. Chelyab. Gos. Univ.. Ekol. Prirodopol'zovanie*, 2010, vol. 8 (189), no. 4, pp. 40–45.
15. Noskov, V.A., Maimur, B.N., and Mozharenko, N.M., Briquetting of fine fraction wastes from mining and metallurgical, and machine-building complexes of Ukraine for utilization in metallurgical aggregates, *Metall. Gornorudn. Proizvod.*, 2002, no. 1, pp. 119–122.
16. Szekely, J., Steelmaking and industrial ecology—Is steel a green material? *ISIJ Int.*, 1996, vol. 36, pp. 121–132.
17. Matsubae-Yokoyama, K., Kubo, H., and Nagasaka, T., Recycling effects of residual slag after magnetic separation for phosphorus recovery from hot metal dephosphorization slag, *ISIJ Int.*, 2010, vol. 50, pp. 65–70.
18. Senk, D., Gudenau, H.W., Geimer, S., and Gorbunova, E., Dust injection in iron and steel metallurgy, *ISIJ Int.*, 2006, vol. 46, no. 12, pp. 1745–1751.
19. Zhibinova, I.A., Shakirov, K.M., Protopopov, E.V., and Shakirov, M.K., Thermodynamic principles in the liquid-phase reduction of oxides in an oxygen converter, *Steel Transl.*, 2009, vol. 39, no. 2, pp. 108–110.
20. Shkoller, M.B., Kazimirov, S.A., Temlyantsev, M.V., and Basegskiy, A.E., Conditioning of coal-enrichment waste with high moisture and ash content, *Coke Chem.*, 2015, vol. 58, no. 12, pp. 482–486.
21. Islamov, S.R., *Energotekhnologicheskaya pererabotka uglya* (Energy-Technological Coal Processing), Krasnoyarsk: Polikor, 2012.
22. Shkoller, M.B., Kasimirov, S.A., Khodosov, I.E., and Ivanov, V.P., Processing of converter slurry by coking with coal, *Coke Chem.*, 2017, vol. 60, no. 2, pp. 80–85.
23. Shkoller, M.B., Protopopov, E.V., and Yur'ev, A.B., *Energotekhnologiya tverdogo topliva* (Energy Technology of Solid Fuel), Novosibirsk: Sib. Otd., Ross. Akad. Nauk, 2015.
24. Ul'yanov, V.P., Bulavin, V.I., and Butenko, A.N., Thermal processing of oil-containing industrial waste to produce marketable products, *Integr. Tekhnol. Energosberezhenie*, 2004, no. 3, pp. 48–53.
25. Ul'yanov, V.P., Zlobin, A.G., Umnov, G.S., Beketova, L.A., Zhilina, N.I., Bolotova, L.D., Dmitriev, V.Ya., Gryzlin, R.M., and Yurkov, G.I., USSR Inventor's Certificate no. 1151768, *Byull. Izobret.*, 1985, no. 15.
26. Taits, E.M., *Koks i zhelezokoks na osnove briketirovaniya* (Briquetted Coke and Ferrocoke), Moscow: Metallurgiya, 1965.

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